

FORMULATIONS OF WATER-BORNE ADHESIVES BASED ON TERNARY BLENDS OF LATEXES

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ABSTRACT

The generally accepted definition of an adhesive is any material used for holding any two surfaces together. Three different polymer latexes derived from natural rubber (NR), Acrylic (Ac) and Vinyl Acetate/Veova (VA/Ve) copolymer emulsions were blended using the principle of simplex lattice design to yield ten compositions. The blends were then used in formulating corresponding number of water-based adhesives each of which was used in making two sets of single-lap adhesive joints for comparative curing under sun and under oven temperature conditions, respectively. Bond strengths of the cured joints were determined using an improvised set-up and, from the results that were obtained, it was observed that bond strengths for joints cured under sun condition were higher than for those under oven-dry condition for all the cases where real values were determined. There were few cases on both sides of the conditions of drying for which the set up was inadequate to produce measurable reading but with the pattern shown in the results, it seem reasonable to conclude that the sun cured adhesive joint based on the blend derived from NR, Ac and VA/Ve blends in the ratio of 1/6:2/3:1/6, respectively, which corresponds to equivalent formulation of oven-cured joint with the highest measurable value of bond strength, is the strongest among all the formulations. This blend was thus regarded as “optimum blend”. Comparison of the bond strength measured from adhesive joint based on the optimum blend with similar value from adhesive joint prepared from a popular commercial wood based adhesive (Top Bond) in Nigeria was made. Interestingly, it was observed that the value of bond strength from the prepared adhesive was higher and more promising. It is thus suggested that sun-curing conditions are more suitable and better recommended than oven-curing conditions for curing the tested adhesives.

KEYWORDS: adhesive, ternary blends, latexes, simplex lattice design, bond strength, adhesive joints.

INTRODUCTION

Adhesive is a substance capable of holding materials together by surface attachment (Panek and Cook, 1991). To be termed an adhesive, a substance must be liquid or tacky semisolid, at least for an instant to contact and wet a surface, and be used in relatively thin layer to form a useful joint capable of transmitting stresses from one substrate to another. Adhesives are used in a wide gamut of applications today which are becoming more and more common replacements for mechanical fasteners such as welds, riveted joints, joints with screws, etc., in products. This development is most visible in the automotive and aviation industries, the home area, the broad paper and plastic markets as well as industry involved in the manufacture of intermediate and final products. Also, in the wood working industry, the direction is toward the industrial use of glued materials and construction instead of nailing or screw joints. The most rapid development is taking place in the building product area, where more efficient joining techniques are needed (Backman and Lindberg, 2004). Mechanical fasteners are, by their nature, discontinuous, and thus cause stress concentrations. Even welds, considered by many to be the best method of attaching metals, are most often fillet or plug weld and, consequently furnish only edge attachment. The adhesively bonded joint, on the other hand, furnishes full film of adhesive over the bonded parts, which results in a more uniform stress distribution. Adhesive bonding in many cases offers the contractor easier installation resulting in savings in construction costs. Adhesively bonded wallboard may require less plastering and sanding. Acoustical tile for residential ceilings can often be installed more quickly by bonding than stapling. Installation batts attached to wall studs can be installed more quickly and with better seal by using adhesives (Panek and Cook, 1991). These are reasons responsible for the phenomenal development of adhesives.

Materials used as adhesives are polymers, which occur either naturally or are synthetic. Some examples in the natural category include cement (inorganic polymer based on silicates), glues, or pastes, waxes, natural resins, gums and asphaltic pitches as hot melt adhesives. Others in the synthetic category are silicone, epoxy, urethane and phenolic resins to mention but a few. Blending of polymers is undertaken by mixing two or more existing

polymers in order to obtain synergy in a single composite formulation. Ternary blends, in particular, are mixtures comprising three component materials that are blended with one another, one of which must be a polymer. Blend usually shows better properties and wider applicability than any of single components from which it is made (Olabisi *et al.*, 1979; Alger and Dyson, 1990; Linares and Acosta, 1997; Krupa and Luyt, 2001; Zeng *et al.*, 2004). The rubber industry as well as commodity plastics producers have used blending so as to continuously improve on the properties of their products and to meet customers' specifications (McDonel *et al.*, 1978; Fox and Allen, 1991). Since blends involve the use of pre-existing materials, avoiding synthesis, they offer pecuniary advantage and time-saving economy. To make them available in viscosity suitable for application on substrates, the polymer or a blend of polymers is dispersed or dissolved in suitable liquid of the formulation, which may be water or an organic solvent, where the necessary additives had been previously added.

Latexes also known as polymer colloids (Sperling, 1992) are dispersions of polymer particles in water. Latexes are obtained either naturally, as for example natural rubber latex from *Hevea brasiliensis*, or by synthesis, with several examples now available. The synthetic ones, more appropriately called emulsions, being usually as products of emulsion polymerization, are prepared from raw materials derived from petroleum and/or coal which are not only non-renewable but also constitute a major source of environmental pollution and, therefore, must be used with great caution. Latexes are known to be environment-friendly materials, which are widely used in formulation of adhesives, coatings, surface finishing, paper, and textiles. They are becoming increasingly important as a consequence of strict regulatory restrictions about solvent emissions and other ecological considerations (Amo *et al.*, 2002; Geurink *et al.*, 1996; Amalvy and Soria, 1996; Topçuoğlu *et al.*, 2006; Makarewicz, 1996). Since latex-based systems are all based on water and without organic solvent content, using only very small amounts to modify final film properties or paint flow and rheological properties, they are of low volatile organic compound (VOC) emission or VOC-free. In addition to reducing direct emissions of solvents, use of latex-based systems avoids dangers such as risk of fire occurrence and workers' exposure to hazards and waste handling problems, environmental pollution, and ozone depletion common with solvent systems (Anonymous, 1987).

This work is focused on the blending of three latexes, namely natural rubber (NR), acrylics, and vinyl acetate-VeoVa10^R (VA/Ve) copolymer. NR latex is obtained from rubber trees, *Hevea brasiliensis*, which is abundantly cultivated in Nigeria and other parts of the world. As an agricultural product, it can easily be grown by farmers to any desired quantity. Besides being cheap, it is biodegradable and hence, does not constitute hazards to the environment. It has excellent resilience and abrasion resistance. However, NR, due to presence of unsaturation in its stem, is thermally unstable and susceptible to oxygen degradation in presence of light which are factors that tend to limit its applications. Acrylics dispersions are known for their good film hardness, resistance properties and adhesions on a number of substrates but, regrettably besides being costly, give rise to flat finishes which, apart from being brittle at low temperature, also have weak solvent resistance (Aznar and Amalvy, 2006). Vinyl acetate-VeoVa10^R (VA/Ve) copolymer emulsion has required hardness/flexibility, excellent gloss, high water resistance, UV resistance and alkali resistance which lead to superior durability (Decocq *et al.*, 1999). However, they are more expensive than acrylics and need to be stabilized by surfactants to be able to exhibit the required hardness/flexibility for formulation of a range of high performance water-based products. The objective, therefore, of this work is firstly to prepare various blends from these latexes in different ratios. Thereafter, the blends are formulated into adhesives which will then be evaluated, in comparison with a known commercial adhesive of similar composition (PURECHEM Top Bond^R), on basis of bonding strengths with wood substrates.

It is hoped that, from the blend of these three latexes, a product that combine all the good characteristics of the three latexes and is better than any single component will be obtained. Given that Nigeria is endowed with abundant natural rubber plantation, the successful employment of rubber latex in ternary blend for adhesive production will be a value-added advantage to rubber and a further incentive to farmers/establishments involved in growing rubber plantation.

EXPERIMENTAL

Materials:

Natural rubber latex (LA-TZ grade) was supplied by Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City; VA-Veova emulsion by NYCIL Ltd, Sango Ota, Nigeria and Acrylic was donated by Chemstar

Paint Nigeria Ltd., Lagos, Nigeria. All these materials were used as received without need for further purification.

Methods:

Total Solid Contents (TSCs) Determinations of the Latexes

The three polymer latexes, as received, were thoroughly stirred and portions from each weighed into three different petri dishes using a Metler weighing balance (Model: 13300D-12951). These were then heated in an oven at fixed temperature of 50°C. After regular intervals the samples were taken out, cooled in a dessicator and then re-weighed. The process was heating, cooling and re-weighing was repeated until constant weights were obtained. The percentage TSCs of each sample was therefore evaluated using the equation below:

$$\% \text{ TSCs} = W_f/W_i \times 100 = (W_3 - W_1)/(W_2 - W_1) \times 100 \quad (1)$$

Where,

W_1 = weight of empty dish

W_2 = weight of dish + sample content before drying

W_3 = weight of dish + sample content after drying

W_i = Actual weight of the wet sample

W_f = Actual weight of the dried sample

A set of three measurements were taken for each sample and the values reported as average total solid contents. Blends Preparation and Adhesive Formulations Procedures

Firstly, based on the previously determined TSCs, the latexes as supplied were subsequently diluted using distilled water to 30% (v/v) aqueous dispersions. The dilution factor was calculated from the following expression:

$$VH_2O = V_i(C_i - C_f)/C_f \quad (2)$$

Where,

V_i = Initial volume of original emulsion taken for dilution

C_i = Initial TSCs of the emulsion before dilution.

C_f = Final TSCs in the diluted emulsion

VH_2O = Volume of water required for dilution so as to yield the final (expected) TSCs.

After the pH of the diluted samples were determined using a pH meter (Model: Kent E/L 704/46), ten different blends of these diluted samples were made. The blending technique employed was based on the principle that the total volume of mixed components for each formulation number is a constant value.

In the blending process, knowledge of the pH differences between the samples was wisely applied in order to prevent premature coagulation of NR component. For blends which involve a component that is acidic, as for example, acrylic and another that is basic as with NR, the latter was initially pre-mixed with ammonia solution to adjust its pH to about 9 in order to prevent coagulation of NR before homogenization. Each of the above blend obtained from the dilute aqueous dispersions were then formulated into adhesives using the recipes shown in Table 2.

Curing conditions

Following their formulations, the adhesives were tested in order to examine their respective bond strengths. Each formulation of the adhesives was first applied to bond two adherends based on single lap joint design as shown in Figure 1. Two sets each of such test samples, one for drying in the air and the second for drying in oven condition at a constant temperature (50°C) for comparative purposes, were made for each of the formulated adhesives.

Bond strength determinations

To date, no adequate nondestructive means of testing adhesive bond is presently available, but techniques are worked out that may prove satisfactory (Panek and Cook, 1991). A simple, effective locally improvised

technique was thus employed to test the adhesive bond strengths of the prepared adhesives, along with a commercial one used for comparison. After the curing process, the procedure used to measure the bond strength of the prepared adhesives involved the clamping of the bonded specimens as schematically shown in Figure 2. One end of the bonded specimen was firmly attached to the flat surface of a table by means of the clamp. On the other end of it, standard weights were gradually applied via a loop until the point of failure of the specimen, which could either be at the bond joint or any other point on the substrate.

The formula used for evaluating the bond strength for the prepared adhesives was determined from the minimum amount of load that would result in failure at the adhesive joint and was evaluated using Equation 1. Similar test procedure was used in determining the bond strength of a commercial adhesive (PURECHEM "Top Bond") for comparing formulated adhesive.

$$\text{Bond strength} = \frac{\text{Force (N) at specimen failure}}{\text{Surface area (m}^2\text{) of contact}} \quad (1)$$

RESULTS AND DISCUSSION

The TSCs of the samples as supplied were found to be 41.21, 50.20 and 53.00 wt. % for NR, VA/Ve and Ac latexes, respectively, and shown graphically in Figure 3. NR has the lowest value of TSCs followed by VA/Ve which is higher and then Acrylic, having the highest value. These differences in TSCs were also reflected in the physical appearances of the samples. In terms of physical appearance, it was observed that the acrylic polymer, which has the highest value of TSCs, was the most viscous, while NR with the lowest TSCs was correspondingly the least viscous of the three. While the TSCs of NR was naturally inherent, those of both acrylic and VA/Ve latexes, being synthetic were determined by their respective manufacturers by the controlled addition of additives during formulation as dictated by specification targets. From literature (Onwueme, 1979), the TSCs of fresh NR latex fall usually around 35wt %. However, through a process of deliberate concentration, which may involve evaporation, centrifuging or creaming, the TSCs of the freshly obtained latex can appreciate to a value of about 60-65wt %. During latex transportation from the field where it is usually collected to the storage tank in the factory, some evaporation could also take place. This can make the TSCs to be above 35% but certainly the effect is not enough to make the value go up to 60-65wt. %. The TSCs of NR used in the present study was found to be 41.21wt %, which was a little above the literature value of 35 wt %. This implies that the concentration effect that resulted to this level of TSCs (41.21 wt. %) of the latex could only be attributed to the evaporation of water and ammonia stabilizer occurring in the latex during transportation from the field to storage site. It is expected that the TSCs of the dispersions affect the bond strengths of the subsequent adhesive bond strengths. To test the reliability of this assumption, the bond strengths of the adhesives based on the individual latexes were compared and found to vary directly proportional with the TSCs as shown in Table 3.

The pH of distilled-water-diluted dispersions of NR, Acrylic and VA/Veova were measured and found to be 10.98, 7.95 and 4.64, respectively. The high pH value of NR is due to the presence of ammonium hydroxide used as a preservative against coagulation of the latex before storage. The acrylic latex (pH, 7.95) is slightly alkaline while VA/Veova (pH, 4.64) is purely acidic. The knowledge of the pH of these latexes is necessary as a guide to determining the proper sequence of blending so that the latex is not coagulated before blending cycle is completed. The dilution of the latexes was undertaken prior to their blending together in order to achieve quick efficient blending process.

The results of bond strengths determined for the formulated and commercial adhesive after curing under the two drying conditions, viz sun and oven drying are shown in Table 4. It was generally observed from the results that bond strengths for joints cured under sun condition were higher than for those under oven-dry condition, for all cases where real values were determined. This is true both for individual component-based as well as blended samples. As seen, among the adhesives based on individual dispersions, the highest bond strength recorded was represented by the component, 0:1:0 (Ac.) under sun-dried process. In case of the blended samples, there were few cases, on both sides of the conditions of drying, for which the set up was inadequate to produce measurable reading. These cases represented those for which applied stress failed to cause adhesive failure on the adhesive joint. For such, it is suggested that the adhesive force at these joints were stronger than the stress applied in order to cause separation at the joints. However, for those that measurable readings were obtained for the blended samples, it was observed that bond strengths from sun-cured conditions were importantly greater than

bond strengths from oven-cured conditions. Going by this observed pattern, it seems logical to conclude that the strongest adhesive joint among all the formulations might as well be the sun-cured adhesive joint based on the blend derived from NR, Ac and VA/Ve blends in the ratio of 1/6:2/3:1/6, respectively. It is observed from the results that the corresponding blend formulation of oven-cured joint gave value of bond strength (48 N/m^2) with the highest measurable reading. We thus regard the blend of this composition of sun-cured sample as “optimum blend”. It is presumed that, if actual reading had been obtained for sun-cured bond strength of adhesive of this blend (NR:Ac:VA/Ve, 1/6:2/3:1/6), the value expected should have been greater than 48 N/m^2 .

The generally lower values of bond strength obtained for adhesives cured in oven conditions in comparison with those of sun conditions might be due possibility that the oven conditions impacts marked ageing effect on the polymer or blend in the adhesive formulation. Ageing would lead to lowering of mechanical integrity and consequently, reduced bond strength as observed. The samples with the abbreviation, “C.N.Ds” against them instead of actual values are those for which the bond strengths were so strong that the test method used could not cause bond failure at their adhesive joints. Thus, it was assumed that the bond strengths, though undetermined, should be correspondingly higher than that of the comparable formulation measured against oven-dried conditions.

CONCLUSIONS

Ternary blends have been prepared from three components namely NR, VA/Veova and acrylic dispersions based on systematic blending ratios. The obtained blends over the entire composition range were used in formulating water-borne adhesives, which were then characterized for bond strengths using an improvised measurement technique. The bond strengths of the prepared adhesives were found to be dependent upon the composition of the latex blends and also curing conditions. Typically, it was observed that the adhesive joints formed as a result of curing under sun drying condition showed bond strengths that were of higher magnitude than for those cured in oven drying condition. The observed differences in bond strengths produced based on conditions of curing have been attributed to ageing effect likely more pronounced in oven condition than in the case with sun drying condition. The highest bond strength (48 N/m^2), using the oven-dried readings as illustration, was observed against a blend composition (1/6: 2/3: 1/6 for NR, Ac, VA/Ve, respectively) comprised of three components. This indicates that improvement in properties has resulted by the blending technique as characteristic (Olabisi *et al.*, 1979; Alger and Dyson, 1990; Linares and Acosta, 1997; Krupa and Luyt, 2001; Zeng *et al.*, 2004). Finally, it was found that the bond strengths of the prepared adhesives showed better promise than that of a popular commercial adhesive (Top bond) used for comparison in this study.

REFERENCES

- Alger M.S.M. and Dyson R.W. (1990) Polymer Blends. In: *Engineering Polymers*, Dyson, R.W. (ed), Chapman and Hall, New York, pp. 20-28.
- Amalvy J. I. and Soria D. B. (1996) Vibrational spectroscopic study of distribution of sodium dodecyl sulphate in latex films. *Progress in Organic Coatings*, 28, 279-283.
- Amo B. del, Romagnoli R., Deya C. and González J.A. (2002) High performance water-based paints with non-toxic anticorrosive pigments. *Progress in Organic Coatings* 45, 389-397.
- Anonymous (1987) “Solvents Limits Proposed Would Cut Exposures”. *Chem. Market Rep.*, p.7
- Aznar A.C. and Amalvy J.I. (2006) Manufacture and testing of waterborne paints by using vinyl latex containing VeoVa10^R monomer. *Latin American Applied Research* 36, 149-154.
- Backman A.C. and Lindberg K.A.H. (2004) Interaction between wood and polyvinyl acetate glue studied with dynamic mechanical analysis and scanning electron microscopy. *Journal of Applied Polymer Science*, 91, 3009-3015.
- Decocq F., Heymans D. and Nootens C. (1999) Veova-based binders for high quality emulsion paints. *Pittura e Vernici* 7, 41-45.

Fox D.W. and Allen R.B. (1991) Compatibility. In: *High Performance Polymers and Composites*, Kroschwitz, J.I. (ed), Wiley, New York, pp. 65-82.

Geurink P.J.A., Dalen L., Ven L.G.J. and Lamping R.R., Analytical aspects and film properties of two-pack acetoacetate functional latexes (1996). *Progress in Organic Coatings*, 27, 73-78.

Krupa I. and Luyt A.S. (2001) Thermal properties of polypropylene/wax blends. *Thermochimica Acta* 372, 137-141.

Linares A. and Acosta J.L. (1997) Tensile and dynamic mechanical behaviour of polymer blends based on PVDF. *European Polymer Journal* 33, 467-473.

Makarewicz E. (1996) Studies on the stability of aqueous emulsions containing linseed oil and alkyd resin modified by linseed oil. *Progress in Organic Coatings* 28, 125-132.

McDonel E.T., Baranwal K.C. and Andries J.C. (1978). In: *Polymer Blends*, Paul, D.R.; Newman, S. (eds) (Vol 2), Academic Press, New York, p.263.

Olabisi O., Robeson L.M. and Shaw M.T. (1979) *Polymer-Polymer Miscibility*, Academic Press, New York.

Onwueme I.C. (1979) *Crop Science*, (Book 2). Cassell Ltd., London, pp 99-100.

Panek J.R. and Cook J.P. (1991) *Construction Sealants and Adhesives* (3rd edn), Wiley, New York.

Sperling L.H. (1992) *Introduction to Physical Polymer Science* (2nd edn). Wiley, New York.

Topçuoğlu Ö., Altinkaya S.A., and Balköse D. (2006) Characterization of waterborne acrylic based paint films and measurement of their water vapor permeabilities. *Progress in Organic Coatings* 56, 269-278.

Zeng M., Zhang L. and Zhou Y. (2004) Effects of solid substrate on structure and properties of casting waterborne polyurethane/carboxymethyl chitin films. *Polymer*, 45, 3535-3545.

Table 1: Schematic representation of the simplex lattice design for blends' formulation

Formulation number	Natural rubber	Acrylic	VA/Veova
1	1	0	0
2	0	1	0
3	0	0	1
4	1/2	1/2	0
5	1/2	0	1/2
	0	1/2	1/2
6	1/3	1/3	1/3
7	2/3	1/6	1/6
8	1/6	2/3	1/6
9	1/6	1/6	2/3
10	1/6	1/6	2/3

Table 2: Ingredients used for the adhesive formulations

Ingredient	Volume fraction (Φ)	Function
Latex	0.875	Film former
Thickener (Natrosol)	0.022	Particles dispersant
Surfactant (Texapon N70)	0.029	Substrate wetting agent
Antifoamer (Paraffin oil)	0.015	Prevents foam build-up
Plasticizer (Glycerol)	0.015	Improves film's flexibility
Filler (CaCO_3)	0.010	Increases bulk
Anti-oxidant (Alkylated phenol)	0.015	Prevents films' oxidation
Curing agent (Sulphur)	0.015	Accelerates adhesive's drying
Sodium benzoate	0.005	Preservative

Table 3: Relationship between adhesive bond strengths and TSCs

Adhesive type	TSCs (wt. %)	Bond strengths (N/m^2)	
		Sun-cured	Oven-cured
NR	50.81	20	16
VA/Ve	63.23	40	36
Acrylic (Ac)	73.00	48	40

Table 4: Bond strengths of adhesive formulated from each blend

Adhesive composition	Bond strength (N/m^2)	
	Sun-dried	Oven-dried
NR:Ac:VA/Veova:		
1: 0: 0	20	16
0: 1: 0	48	40
0: 0: 1	40	36
1/2: 1/2: 0	36	28
1/2: 0: 1/2	32	24
0: 1/2: 1/2	C.N.D.	36
1/3: 1/3: 1/3	40	32
2/3: 1/6: 1/6	32	20
1/6: 2/3: 1/6	C.N.D	48
1/6: 1/6: 2/3	C.N.D.	40
"Top Bond ^R " (commercial)	52	48
C.N.D. = could not be determined		

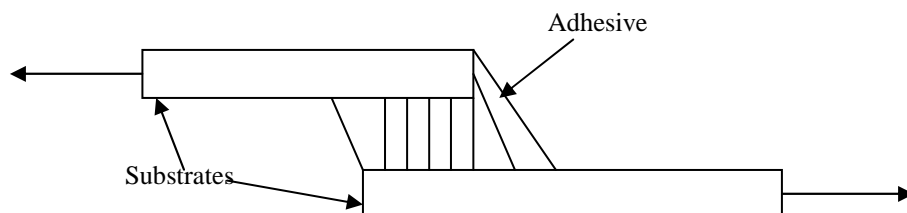


Figure 1: Single-lap joint design for bonding with the adhesives

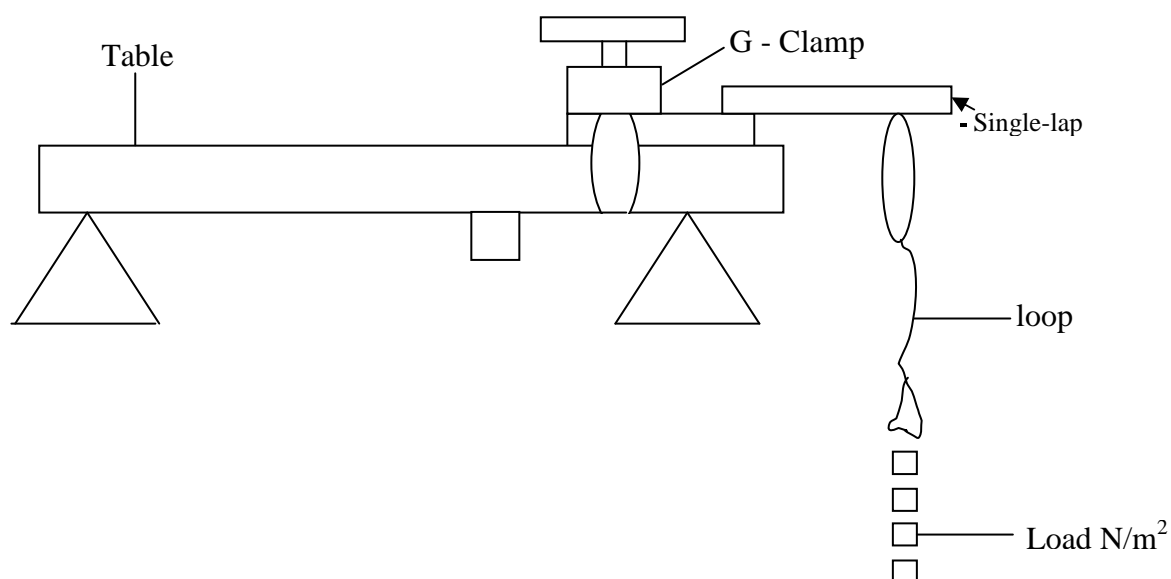


Figure 2: The device used for measurement of adhesive bond strength.

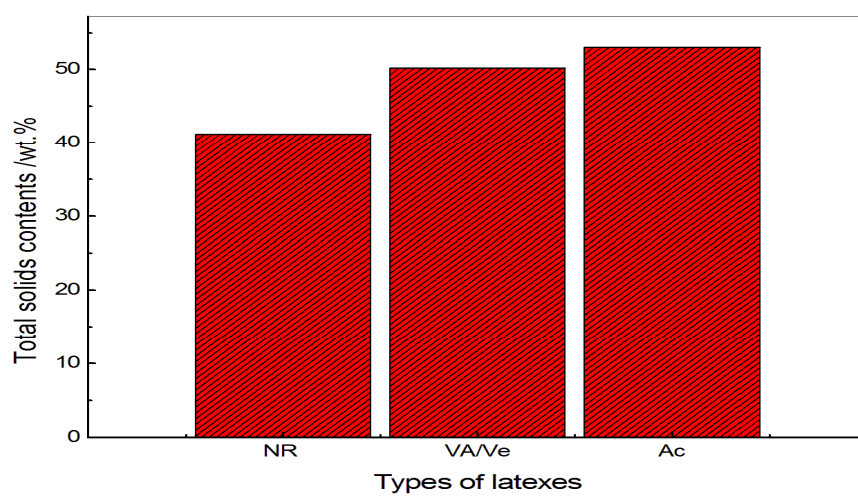


Fig.3. Histogram of TSCs of individual latexes